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A Study of the Antimony-Tin Separation

Chemical Engineering

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A STUDY
OF THE
ANTIMONY-TIN SEPARATION

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

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John Maurice Welch

ENTITLED A Study of the

Antimony-Tin Separation

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

in Chemical Engineering

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A STUDY
# of the
ANTIMONY - TIN SEPARATION

I INTRODUCTION.

The customary methods for the separation of antimony and tin are well known and are very satisfactory, in that they give accurate results. To obtain this accuracy, however, it is necessary that the operator have had some little experience in the analysis for the metals, as well as practice in manipulation according to the procedure that is to be used. However, practice and experience will not bring the desired result, unless the operator uses care in following the procedure exactly as it is given. Deviations in manipulation, however slight, are apt to cause great deviations in the accuracy, and accuracy is the prime prerequisite for all analyses. Beginners are, as a rule, not given to careful following of outlined procedure and as a result they get into numerous difficulties, and are at a loss to explain why it is that they do not obtain correct results. They do not see the importance of using the amounts of the reagents given in the directions, and only those amounts. If the amount stated will bring about the desired result, why will not a little more hasten the process? The beginner brings all sort of argument to support his theory, but when that theory is put to the test in the course of the analysis,

it proves to be grievously at fault. It is in an endeavor to discover a more simple method, which will not place so many difficulties in the nature of exact procedure in the path of the beginner, that this work was carried out.

The usual method for the separation and analysis for antimony and tin, as determined by Arthur A. Noyes and William C. Bray,[1] depends for its value upon the relative solubility of the sulphides in different concentrations of hydrochloric acid. The method is very accurate and in the hands of a practiced and careful operator will detect as little as two milligrams of tin, the usual accuracy being, however, about five milligrams. When, however, the method was used by beginners, it was found that many errors resulted. The statistics[2] give tin as the metal of the group which gives the greatest amount of trouble, it being missed in 20.2% of the cases examined; arsenic was very close, being missed in 18.4% of the cases; while antimony was seldom missed, the percentage being but 0.9%. The actual figures are, perhaps, even a little higher in respect to the arsenic and tin, for in the compilation of the data only the work of those passing the courses in qualitative analysis was taken into consideration.

According to this system the metals of the second

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[1] Jour.Am.Chem.Soc., v 29, no 2, p 137 (1907)

[2] From the reports of the students in qualitative analysis at the University of Illinois during the summer session of 1914 and the first semester courses of the school year of 1914-1915. From 150 to 200 reports were examined.

group are precipitated in the usual manner by passing hydrogen sulphide into a solution made slightly acid with hydrochloric acid. The metals of the copper group are then separated from those of the tin group by treatment with yellow ammonium sulphide,[1] which dissolves the the arsenic, antimony and tin sulphides with the formation of the complex salts, $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$, and $(NH_4)_2SnS_3$. The acidification of this solution reprecipitates the metals in the form of their 'ic' sulphided and they are filtered out and dried by suction as As_2S_5, Sb_2S_5, and SnS_2. Up to this point there is no great difficulty encountered but from this point on the beginners' troubles are almost without number.

The precipitate is then treated with exactly 10 cc of concentrated hydrochloric acid (sp.gr. 1.2) and warmed for ten minutes on a water-bath. This treatment causes the antimony and tin to go into solution as antimony trichloride, $SbCl_3$, and stannic chloride, $SnCl_4$, the arsenic sulphide remaining unchanged. The solution is then diluted with 5 cc of water and filtered, after which the residue is washed with an additional 5 cc, the washings being added to the filtrate, and the volume of the filtrate brought to 50 cc by the addition of 30 cc of water.

The filtrate is then heated to about 90° and saturated

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[1] The addition of a small amount of KOH to the $(NH_4)_2S_x$ hastens the process materially.

with hydrogen sulphide for five minutes, keeping the temperature at 90°. If no precipitate appears, add 5 cc of water and again saturate, keeping the temperature constant. An orange-red precipitate, antimony sulphide, Sb_2S_3, shows antimony. This is filtered off, dissolved in about 2 cc of hydrochloric acid and tested for antimony by placing a small piece of platinum foil in the solution and then placing upon that a small piece of tin. A black deposit of metallic antimony appearing on the platinum shows that the metal is present. As a precaution it is advisable to further dilute the filtrate after the first precipitation with an additional 5 cc of water and again saturate hot with hydrogen sulphide, adding any precipitate formed to the first precipitate obtained. The filtrate is then tested for tin.

If this process is carried out with care, a very perfect separation of the antimony and tin is obtained. If the solution, thru any error, be too strongly acid, a small amount of antimony will fail to precipitate and will escape detection. If the solution is not acid enough a part of the tin will precipitate with the antimony to give a brown colored precipitate, the same being true if the temperature is not kept at approximately 90°. Small amounts of tin in the presence of large amounts of antimony will give a very decided brown color to the precipitate.[1]

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[1] See "Brown Precipitate", page 6.

For the purpose of precipitating the tin, the filtrate from the antimony precipitation is diluted with 20 cc of cold water, cooled to about 25°, and saturated with hydrogen sulphide. The tin is precipitated as the yellow stannic sulphide, SnS_2, which is filtered off and dissolved in a little hydrochloric acid, with the formation of stannic chloride, $SnCl_4$.

The difficulty incident to the filtration of stannic sulphide is one of the greatest troubles that the beginner has to overcome. The precipitate is finely divided and very often is in the colliodal state and, like all precipitates of that nature, is very hard to handle. The precipitate will repeatedly pass thru the filter and it is necessary to filter several times before the filtrate will run clear.

The strongly acid solution of $SnCl_4$ is then treated with a small excess of metallic zinc and the action allowed to proceed until the zinc is almost completely dissolved. The tin is reduced to the metallic state and is deposited as a spongy, gray mass, which is often overlooked by the beginner and thrown away. The tin and the excess of zinc are separated from the solution by decantation and completely dissolved in a little concentrated hydrochloric acid, diluted with one-half the volume of water and at once poured thru a filter into a few cubic centimetres of mercuric chloride, $HgCl_2$, solution. A white precipitate of mercurous chloride, Hg_2Cl_2, indicates the presence of tin. The mercurous chloride is formed according to the reaction: $SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$

II EXPERIMENTAL.

The "Brown Precipitate":-

In the description of the precipitation of antimony mention was made of the 'brown precipitate' formed when a small amount of tin precipitated with the antimony. From the work in the laboratory it was noticed that in the majority of cases where antimony and tin were both present, the beginner obtained such a precipitate. The formation was, of course, due to an error on the part of the operator, but the repetition of it led to an investigation of its value as an indication of the presence of tin.

"Tin Salt", $SnCl_2 \cdot 2H_2O$, was used as the source of tin and an attempt was made to oxidize this by the addition of bromine to the solution. In the first attempts the bromine was added after the precipitation and for some reason the oxidation was very irregular, some of the samples being oxidized while others were left unchanged, with the result that the precipitates formed by the second saturation with hydrogen sulphide were of various colors.[1] The effect of adding the bromine before the saturation with hydrogen sulphide was next tried and it was found that stannous tin could be easily oxidized to the stannic condition, the excess of the bromine being removed by boiling before the introduction of the hydrogen sulphide. The method used was practically the same as

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[1] Stannous sulphide, SnS, is of a deep brown color, in some cases it is almost black.

that of Noyes and Bray, with the following alteration:

The filtrate containing the antimony and tin was diluted to a volume of 70 cc, with an acid content equal to 10 cc of concentrated hydrochloric acid, and then saturated hot and cold with hydrogen sulphide. The relative concentrations in the test solutions of the two metals are given in Table No. 1 and the results of the investigation follow.

With the ratio of the antimony to the tin varying as given in solutions "I" to "U", inclusive, the brown color was easily recognized, being most sharply defined in the region indicated by solutions "K" to "S", inclusive. When the antimony was in greater proportion than indicated in solution "I", it was extremely difficult to discover a marked difference between the color of the precipitate and the color of a precipitate of antimony sulphide alone. When the proportion of the tin exceeded that given in solution "U", the color was so decidedly yellow that the presence of tin could not be doubted. The presence of the antimony being indicated by the red precipitate first formed when the hydrogen sulphide was passed into the hot solution.

In an endeavor to discover the limits within which the beginner would be able to detect the gradation in color, the flasks were renumbered and a beginner from the laboratory was asked to arrange them in the descending order of the brown color of the precipitates. This was repeated a number of times and in every case the beginner arranged the flasks con-

TABLE No. 1

COMPOSITION of SOLUTIONS
for the
INVESTIGATION of "BROWN PRECIPITATE"

Number	Grams Sb per cc	Grams Sn per cc	Sb/Sn Ratio
A	0.00630	0.00032	20/1
B	0.00598	0.00032	19/1
C	0.00566	0.00032	18/1
D	0.00534	0.00032	17/1
E	0.00502	0.00032	16/1
F	0.00470	0.00032	15/1
G	0.00438	0.00032	14/1
H	0.00406	0.00032	13/1
I	0.00374	0.00032	12/1
J	0.00352	0.00032	11/1
K	0.00320	0.00032	10/1
L	0.00288	0.00064	9/2
M	0.00256	0.00096	8/3
N	0.00224	0.00128	7/4
O	0.00192	0.00160	6/5
P	0.00160	0.00192	5/6
Q	0.00128	0.00224	4/7
R	0.00096	0.00256	3/8
S	0.00064	0.00288	2/9
T	0.00032	0.00320	1/10
U	0.00032	0.00352	1/11
V	0.00032	0.00374	1/12
W	0.00032	0.00406	1/13
X	0.00032	0.00438	1/14
Y	0.00032	0.00470	1/15

Note: Solutions "A" to "K" gave red to red-brown precipitates, "K" to "S" were decidedly brown, while the precipitates from solutions "R" to "Y" varried from a clay-brown to a decided yellow.

taining the precipitates from the solutions "K" to "S", inclusive, in the order of the decreasing antimony-tin ratio.

From this it would appear that when the ratio of the antimony content to the tin content lies between the values of 10/1 and 1/10, inclusive, the color of the precipitate formed by the action of hydrogen sulphide upon the solution containing the equivalent of 10 cc of concentrated hydrochloric acid to 70 cc is a very valuable indication of the presence of tin.

The Magnesium Separation:

An interesting method for the determination of tin without the trouble of separating it from the antimony is the method worked out by C. Pertusi and E. Gastaldi.[1] The basis for the method is the power of metallic magnesium to reduce certain metallic sulphides, among which is tin sulphide. A brief description of the process follows:

A part of the precipitate of the combined sulphides of antimony and tin is suspended in a little water with about twice its weight of powered magnesium, shaken for a few seconds, and then filtered. The magnesium quickly reduces the tetravalent tin to the metallic state. The residue on the filter is then taken up with a little concentrated hydrochloric acid

[1] Rend.soc.chim.ital., v 4, p 83 (1914)
thru C.A., v 9, no 5, p 572 (1915)

and the resulting solution poured into mercuric chloride. A white precipitate of mercurous chloride confirms the presence of tin. The sulphides of antimony are also reduced but as the resulting products have no action on the mercuric chloride they do not in any way effect the value of the indication.

This method was tried in the analysis of the same solutions as are given in table No. 2, and it gave the same results as the method using test-lead for the reducing agent. The use of magnesium, however, is slightly more economical in the matter of time and for a quick determination of the tin it could be profitably employed. The presence of antimony would still have to be confirmed by one or the other of the customary methods. Since this point is taken care of in the oxalate separation preference was given to that method.

The Oxalic Acid Separation:

When the modified Noyes-Bray method is used, the color reaction for the indication of tin is obtained, but the problem of separating the antimony from the tin still remains. Mention has been made of the difficulty that beginners have in bringing this about and, in an endeavor to overcome the difficulty, use was made of the principles worked out by F. W. Clarke [1] for the quantitative separation of the metals.

The value of this method depends upon the fact that

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[1] Chem.News, v 21, p 124.

TABLE No. 2

COMPOSITION of SOLUTIONS
for the
INVESTIGATION of OXALIC ACID SEPARATION

(All solutions have a uniform volume of 70 cc)

Solution	Total grams Sb	Total grams Sn	Sb/Sn Ratio
A	0.0233	0.0012	20/1
B	0.0175	0.0012	15/1
C	0.0233	0.0023	10/1
D	0.0210	0.0023	9/1
E	0.0186	0.0047	8/2
F	0.0164	0.0071	7/3
G	0.0140	0.0094	6/4
H	0.0116	0.0118	5/5
I	0.0093	0.0142	4/6
J	0.0070	0.0165	3/7
K	0.0047	0.0189	2/8
L	0.0023	0.0212	1/9
M	0.0023	0.0236	1/10
N	0.0012	0.0177	1/15
O	0.0012	0.0236	1/20

Note: In every case positive tests, becoming fainter as the dilution increased, were obtained for both metals.

antimony is completely precipitated from a solution containing oxalic acid, while stannic salts are not. Stannous salts, however, are decomposed by the oxalic acid, to give the insoluble, crystalline stannous oxalate, so care must be taken to have all of the tin in the stannic condition.

In order that this method may be used quantitatively it is necessary that the combined amount of the two metals does not exceed 0.3 gram and, as this amount is very seldom if ever exceeded during the course of a qualitative analysis, the separation should be very exact. The oxalic acid is added in the proportion of 5 grams of the acid for every 0.1 gram of the combined metals and the tartaric acid, to the amount of ten times the maximum amount of the combined metals. The solution is heated almost to boiling and the antimony is precipitated as the pentasulphide from the hot solution.

The first attempt was in the nature of a reversal of the Clarke method, in that the antimony and the tin were to be precipitated together to give the color reaction and the SnS_2 part of the precipitate afterwards redissolved by the addition of the given amounts of oxalic and tartaric acids.

The results were not as expected. The tin sulphide dissolved as was desired, but the antimony sulphide also dissolved, and the analysis was apparently in the same stage as before the first precipitation, except that the operator had the benifit of the indication of the colored precipitate. A

resaturation of the solution with hydrogen sulphide gave, however, a very complete separation of the two metals, the antimony being precipitated as the orange colored sulphide, while the tin remained in solution. An attempt was then made to test for the presence of tin in the filtrate from this last precipitation, without first going thru the process of neutralizing the oxalic acid present and then precipitating the tin as the stannic sulphide.

The method used was to take from 5cc to 10 cc of the filtrate, add to it an excess of test-lead and boil for from one to two minutes. The solution was then poured thru a filter into a few cubic centimetres of a solution of mercuric chloride, $HgCl_2$. If tin was present the stannous chloride, $SnCl_2$, formed by the reduction with the lead, would reduce the mercuric chloride with the precipitation of mercurous chloride, Hg_2Cl_2. The presence of the rather large amounts of hydrochloric acid would tend to the formation of a small amount of lead chloride, $PbCl_2$, but as this is insoluable in cold water it could be eliminated by cooling before pouring thru the filter into mercuric chloride.

The results obtained seemed to justify additional investigation and the series of solutions given in Table No. 2 were analized by this method, which was changed slightly by the addition of a small amount of hydrogen peroxide to aid in dissolving the brown precipitate. The procedure as it was finally developed was as follows:

III PROCEDURE

The filtrate from the arsenic separation, containing the equivalent of 10 cc of concentrated hydrochloric acid (sp.gr. 1.20) is diluted to a volume of 70 cc and then saturated with hydrogen sulphide, first hot and then cold. The color of the resulting precipitate is then noted, a brown color being an indication that tin is present, after which 10 grams of oxalic acid and 5 cc of hydrogen peroxide are added and the solution heated until the precipitate is completely dissolved, and then boiled for two to three minutes to decompose any excess hydrogen peroxide. The hot solution is then saturated with hydrogen sulphide and the resulting precipitate of antimony sulphide filtered off and tested for antimony according to the usual procedure of Noyes and Bray.[1] The filtrate containing the tin in solution is treated as follows:

From 5 cc to 10 cc of the filtrate are boiled with an excess of test-lead for from two to three minutes after which the solution is quickly cooled and poured thru a filter into a solution of mercuric chloride. A white precipitate of mercurous chloride indicates the presence of tin. If there is any doubt of the presence of mercurous chloride, pour the contents of the tube containing the substance upon a filter, wash once or twice with a little water and then pour ammonium hydroxide upon the residue. A black stain, a mixture of metal-

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[1] See page 4.

lic mercury and mercuric amine, $NH_2 \cdot Hg \cdot Cl$,[1] shows the presence of mercurous mercury.

When the solutions given in Table No. 2 were analized, using the method just described, no difficulty was experienced detecting the presence of either tin or antimony. In the case of tin it was not found absolutely necessary to use the ammonium hydroxide test for the confirmation of the presence of mercurous chloride , although it was used in the case of the solutions poor in tin. These results would indicate a sensitiveness far greater than the analytical procedure would demand, for according to the statement of the authors,[2] the method of Noyes and Bray will not detect an amount of tin less than two milligrams, while this confirmatory test will respond to as little as 0.5 of a milligram.

IV SUMMARY

1. It was found that the color of the precipitate formed by the simultaneous precipitation of antimony and tin sulphides was a very valuable indication of the presence of tin.

2. That the use of powdered magnesium as the reducing agent in the reduction of tin sulphide is very rapid and that the method using this reduction is accurate. The failure of the method to provide for the determination of the antimony

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[1] Barfoed; J. prakt. Chem., v 39, p 211 (1889)

[2] Jour.Am.Chem.Soc., v 29, no 2, p 186 (1907)

is against its use by beginners.

3. That the use of metallic lead as the reducing agent in the reduction of stannic chloride is very satisfactory and that the method using this mode of reduction is accurate and permits sufficient latitude of manipulation to make the method desirable for the use of the novice.

4. That the use of oxalic acid as a preventative of the precipitation of tin sulphide is to be recommended and that the method making use of this property is simple and does not require undue care in obtaining satisfactory conditions for its success.

5. That the oxalic acid method as outlined is accurate, in that it will detect the presence of very small amounts of the metals. That it does not require an undue amount of attention to detail of manipulation and as it also avoids the difficult filtration of tin sulphide it is very desirable for use by a novice.

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